

Adhesion Tension Values of Different Types of Carbon Black against Water and against Benzene

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
Carleton N. Smith
Ann Arbor
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C. N. S.

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COMMERCIAL carbon blacks from different sources exhibit widely different properties. Numerous attempts have been made to account for the diversity in properties of such carbons. The seemingly more plausible theories attribute the diversity to differences in (a) crystal structure, (b) effective surface area, and (c) "activity." The third factor is, however, largely dependent upon either or both of the others.

X-ray studies have contributed much to our information concerning crystal structure of the different modifications of carbon. The diamond and graphite are generally accepted as being structurally distinctive forms. Opinions differ as to the structure of the so-called amorphous or microcrystalline form (14), though much of the evidence points to a definite crystalline structure for it (1). Microcrystalline carbon may, according to some investigators, appear in more than one form—as, for example, alpha and beta modifications (?).

Effective surface area of carbon depends not only upon the degree of subdivision, which may be regulated by soot deposition or by grinding and dispersion of massive carbon, but also upon the degree of surface roughening, as by pitting, etc., or upon the number and size of micropores which may be present.

The high "activity" of certain carbons has been attributed (1) to crystal structure, (2) to specific (effective) surface area, and (3) to the presence of impurities. It has been found (13) that ash-free graphite adsorbs succinic acid but leaves methylene blue untouched. Diamond powder adsorbs in the reverse order. Carbon black (methane soot) behaves like diamond, and activated anthracite like graphite. It thus appears that the precise crystal structure of a solid is important in determining its activity. The work of Miller (12) has gone far to prove that activation of carbon does not necessarily require the presence of impurities, as has often been maintained. On the contrary, it has been shown (5) that the presence of "impurities" on the surface tends rather to decrease the adsorptive capacity of carbon for other substances, inasmuch as the already adsorbed impurity has used up part of the adsorption surface. The conclusion seems justified that activity is largely a function of surface area.

This view has been further substantiated by work in this laboratory on heat of wetting of carbon by binary liquid mixtures (3). Recent unpublished work on adsorption by Bartell and Miller has shown that a direct relationship exists between adhesion tension and adsorption when a given solid is used with different liquids. Adhesion tension may be considered to represent the degree of wetting of a solid by a liquid (2, 4). It is a measure of the change in free surface energy per unit area which occurs when a solid against air (or gas) interface is replaced by a solid against liquid interface. It is numerically equal to the difference between the surface tension of the solid, S_1 , and the interfacial tension solid against liquid, S_{12} , and may be expressed by the equation:

$$A = S_1 - S_{12}$$

Since the adhesion tension is a measure of the change of free surface energy per unit area which occurs when a solid surface is wetted by a liquid, determination of adhesion tension alone cannot serve to determine the fundamental difference between two carbons of different activity.

If, however, adhesion tension values were obtained for a series of different carbons against several different liquids, one might have good evidence as to whether the difference in the adhesion tension values were due to differences in crystal structure or to the presence of adsorbed impurities. In case the differences were due to crystal structure, a uniform difference in the adhesion tension values might be expected for a given series of carbons against each of different liquids. If, on the other hand, the differences were due to adsorbed impurities, less of uniformity in the adhesion tension values for the different series should be expected. It is probable that some of the liquids would not be able to displace the adsorbed impurities, while other liquids would displace them and in so doing would carry the system to a lower energy level. As a result one might find that every one of a given series of carbons would give nearly the same adhesion tension values with one liquid but differing values with another liquid.

A high adhesion tension represents a large free-surface-energy decrease, which may be due either to a definite and high energy decrease at each of many different adsorption points or to a relatively higher energy decrease at each of fewer adsorption points. If the total surface area is the same for different samples of a given carbon, a lower adhesion tension of one means that (1) fewer adsorption points exist as a result of altered crystal structure, (2) fewer available adsorption points exist on the surface of the carbon, as the result of previous adsorption on a portion of the surface, or (3) the energy decrease upon wetting is for some reason less at each of the adsorption points. Should a given carbon be subjected to heat treatment, any change in adhesion tension shown by this carbon would then be due to:

(1) Difference in crystal structure or change in lattice energy of the carbon constituting the surface.

(2) A difference in the amount of adsorbed impurities per unit area as, for example, adsorption or desorption of hydrocarbons, etc., formed through decomposition.

(3) The formation of a highly roughened or porous surface which might alter somewhat the surface tension of the carbon or the interfacial tension of the carbon-liquid system. It is conceivable that the interfacial tension of a highly pitted or highly roughened surface would be slightly different from that of a plane surface of the same solid.

Experimental Method

The method developed by Bartell and Osterhof was used to determine the adhesion tensions of water and of benzene against seven commercial carbons. The method depends on the measurement of the pressure set up when a given liquid displaces air or a second liquid from a membrane of finely divided solid material packed in a displacement cell.

High displacement pressures were obtained with nearly all of the carbon systems studied. Compressed nitrogen was used to secure a pressure balance and the pressures were measured by a standard gas-pressure gage graduated in kilograms per square centimeter. A system under pressure is shown in Figure 1. A primary gage (Schaeffer and Bundenburg) was used for calibration.

Carbons Studied

Inasmuch as the seven carbons chosen for investigation were prepared by different methods, it was believed that they might give different adhesion tension values against a given liquid. Since these carbons are samples from competitive manufacturers, it is not possible to give the exact methods of preparation in this paper. Carbon A is a lampblack, and was obtained as a smoke by the combustion of a specially distilled oil. Carbon B was prepared by the thermal decomposition of Louisiana natural gas. Carbon C was from the same source, but was decomposed in the absence of air. Carbons D, E, F, and G were channel or gas blacks, D was a rubber black, E and F were ink blacks, and G was a color black.

Preparation of Carbons

When tested in the original condition, carbons D, E, F, and G were readily wetted by water and formed a suspension when placed in water. Carbons A, B, and C did not appear to be wetted at all, but remained floating on the water surface. This was due to a surface contamination of the carbon. It was necessary to remove most of the adsorbed substances before any displacement pressure involving use of water against air or nitrogen could be obtained.

The treatment of the carbons for the first series of displacement measurements consisted simply in heating them in covered porcelain crucibles to 700° C. in an electric muffle.

No attempt was made to exclude the air during the half hour that the carbons were held at this temperature. Table I gives the adhesion tension values for the carbons treated in this manner.

Table I—Pore Radii, Contact Angles, and Adhesion Tension Values Calculated from Displacement Pressure Data

(Carbons heated at 700° C. in muffle)

CARBON	AV. PORE RADIUS 10 ⁻⁶ cm.	Θ_{13}	A_{13} Dynes per cm.	A_{12} Dynes per cm.
A	7.93	39° 34'	55.55	82.40
B	7.80	45° 43'	50.34	80.47
C	2.26	55° 07'	41.22	72.19
D	1.73	53° 02'	43.34	70.50
E	1.90	47° 02'	49.13	81.08
F ^a	1.83	55° 37'	40.72	65.96

Θ_{13} = contact angle water against carbon

A_{13} = adhesion tension water against carbon

A_{12} = adhesion tension benzene against carbon

^a Carbon F was packed into the displacement cell at a pressure of 159.2 kg. per sq. cm. The other carbons were packed at 238.7 kg. per sq. cm.

In the preparation of the carbons for this group of experiments the conditions were not closely controlled. Surface reactions undoubtedly took place between the carbons and atmospheric oxygen. Some preferential oxidation may have occurred, and a part of the hydrocarbons present may have been removed thereby. It is also possible that oxygen-containing compounds were adsorbed on the carbon surface even at this temperature. It was interesting to note that all the carbons could be wetted by water after the heat treatment.

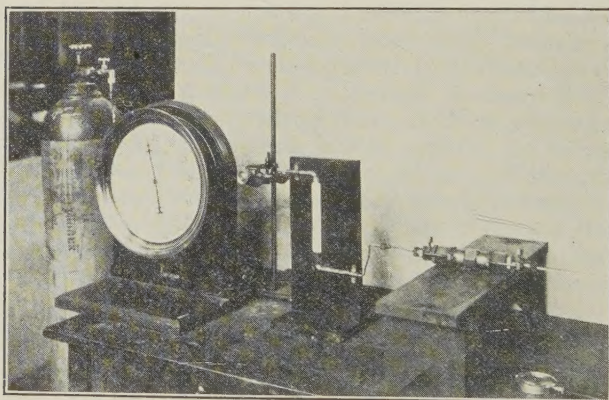


Figure 1—Apparatus for Displacement Pressure Measurements

Different investigators have studied the volatile constituents removed from carbon black by heating. Johnson (11) found that the amount of volatile matter removed at 955° C. ranged from 4.00 to 12.63 per cent for five different carbons. Relatively small amounts of gases were removed at 700° C. He believed that a temperature of 955° C. was

not sufficient to remove all of the adsorbed material. Hulett and Cude (10), in coöperation with the Bureau of Mines, found that gas given off by carbon black heated to 445°C . was chiefly carbon monoxide and carbon dioxide together with some nitrogen. Evidently hydrogen is not liberated until a higher temperature is reached. The appearance of hydrogen would indicate decomposition of hydrocarbons with the possibility of deposition of new carbon on the original surface.

A different and more exact treatment was given the carbons for the second group of adhesion tension measurements. They were heated at 450°C . for a half hour in the muffle. This preliminary treatment was intended to remove most of the moisture and the more highly volatile compounds held on the carbon surface. The carbon was transferred to a

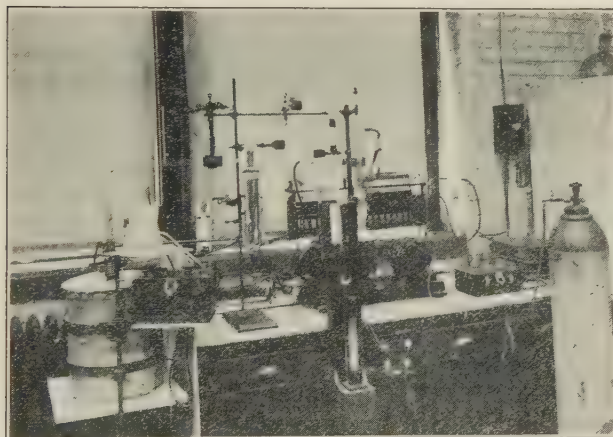


Figure 2—Furnace and Vacuum Apparatus

2-liter clear quartz flask which was attached to a vacuum line. It was then evacuated down to 2 microns of pressure and heated at 500°C . under vacuum for 12 hours. (Figure 2) The flask was allowed to cool and the pressure was then less than 0.1 micron. Oxygen-free nitrogen was admitted until atmospheric pressure was reached. The carbon was again highly evacuated and heated at 500°C . for 12 hours. The applied vacuum should aid in the removal of adsorbed material and should tend to eliminate surface reactions that otherwise might occur at this temperature.

It was necessary to prepare samples of these carbons thoroughly wetted with benzene and with water. This was done by admitting these liquids to different samples while they were still under high vacuum but after they had been allowed to cool to room temperature. In each case the liquid was directed onto the carbon through a capillary tube

(about 25 cm. long) which was insealed into the vacuum line just above the quartz flask. The sealed tip of this tube was broken off under the surface of the liquid. The diameter of the capillary (approximately 0.5 mm.) was such that the liquid was drawn into the flask at a satisfactory rate.

Pressure of Packing

It was found necessary to vary the pressure with which the different carbons were packed into the displacement cells. For a coarse carbon relatively low packing pressures (79.6 kg. per sq. cm.) gave reproducible adhesion tension values; for a comparatively fine carbon pressures four or five times as great were necessary. Table II shows the constancy of the values obtained for a coarse carbon at low pressures and shows that higher pressures are necessary for a finer carbon.

The pore radius decreases as the packing pressure is increased. This is to be expected, for a greater packing pressure will force the carbon particles more closely together and the interstices between the particles will become smaller. Low packing pressures did not hold the finer carbons firmly in place. A pressure of 79.6 to 159.2 kg. per sq. cm. for carbons F and G left them in the state of a loose powder. Higher packing pressures held them rigidly in place and reproducible adhesion tensions were obtained. These values were therefore taken as being truly representative of the adhesion tensions for water and for benzene against the carbons.

Table II—Adhesion Tension Values of Carbon Blacks

PACKING PRESSURE	DISPLACEMENT PRESSURE BENZENE-AIR	PORE RADIUS	A_{12}	A_{13}
Kg. per sq. cm.	Grams per sq. cm.	10^{-6} cm.	Dynes per cm.	Dynes per cm.
HIGH PRESSURE OF PACKING NOT NECESSARY—CARBON A				
79.6	4370	13.18	55.59	82.55
159.2	5730	10.05	55.16	82.52
238.7	6500	8.86	55.33	82.49
318.3	7220	7.98	55.32	82.67
HIGH PRESSURE OF PACKING NECESSARY—CARBON C				
79.6	18280	3.15	21.99	56.45
159.2	24050	2.40	31.77	65.16
238.7	27510	2.09	35.76	69.24
318.3	29270	1.97	36.00	69.44
477.5	32270	1.78	35.54	68.95

Note—The packing pressure gage was calibrated in pounds per square inch. The values registered by it do not represent the true pressure delivered by the hydraulic press on the packing plunger. The area of the packing plunger and the lever effect which the supporting frame exerts on the plunger must also be taken into account. By multiplying the gage value by the factor 0.07958, the delivered pressure reading in kilograms per square centimeter is obtained. Thus, gage pressures of 1000, 2000, 3000, 4000, and 6000 pounds per square inch which were actually read in packing correspond to delivered pressures of 79.6, 159.2, 238.7, 318.3, and 477.5 kilograms per square centimeter, respectively. These values are recorded in the tables.

Effect of High Temperature and Evacuation

A third group of experiments was carried out to determine the effect of higher temperature treatment together with

longer evacuation upon the adhesion tension values. Carbons A, C, and E were chosen for this work. They gave the highest, the lowest, and an intermediate value, respectively, in the preceding experiments.

Table III—Adhesion Tension Values of Different Carbon Blacks Heated and Evacuated at 500° C.

(Displacement measurements at 25° C.)

CARBON	AV. PORE RADIUS 10^{-6} cm.	Θ_{13}	A_{13} Dynes per cm.	A_{12} Dynes per cm.
A	7.98	39° 52'	55.32	82.67
B	7.18	51° 06'	45.26	74.57
C	1.78	60° 27'	35.54	68.95
D	1.35	51° 24'	44.97	72.36
E	1.36	52° 43'	43.67	72.94
F ^a	1.16	54° 27'	41.90	66.87
G ^a	0.763	70° 09'	24.47	58.71

^a Values obtained with carbons F and G are questionable. The carbons were so fine that the displacement pressure method could not be depended upon to give correct pore radii values.

The treatment of the carbons was the same as that in the preceding group of experiments, except that they were heated at 1000° C. for periods of 24 and 96 hours. Table IV gives these adhesion tension values together with those at 500° C.

The adhesion tensions of water and of benzene against carbon A both showed slight decreases when this carbon was subjected to a higher temperature and evacuation for a longer time. A possible explanation for this decrease is that the crystal structure of the original carbon was altered. It seems more probable, however, that the decrease was caused by "cracking" of adsorbed hydrocarbons which liberated small amounts of carbon of different structure. Chaney (6) has found that an "inactive" form of carbon is liberated

Table IV—Adhesion Tension of Carbons after Heat Treatment and Evacuation

TEMPERATURE ° C.	HEATING TIME (UNDER VACUUM) Hours	PORE RADIUS 10^{-6} cm.	Θ_{13}	A_{13}	A_{12}
CARBON A					
500	24	7.98	39° 52'	55.32	82.67
1000	24	7.45	43° 32'	52.26	80.18
1000	96	7.25	44° 39'	51.28	79.03
CARBON C					
500	24	1.78	60° 27'	35.54	68.95
1000	24	1.82	60° 03'	35.99	70.24
1000	96	1.77	60° 39'	35.33	69.46
CARBON E					
500	24	1.36	52° 43'	43.67	72.94
1000	24	1.32	53° 00'	43.38	77.11
1000	96	1.33	52° 56'	43.45	77.05

at 900° C., which deposits upon the surface of the original carbon.

The adhesion tension values for carbon C against both water and benzene remained practically unchanged; hence we assume that no fundamental change occurred at the higher temperature.

The adhesion tension values for water against carbon E

remained practically unchanged, but those for benzene showed an increase. Although an interpretation of results is admittedly but a matter of speculation since the specific surface areas of the different carbons are unknown, it seems logical to assume that heat treatment did not appreciably alter the crystal structure of the original carbon, but instead did alter the nature of adsorbed hydrocarbons, so that at least some of the final adsorption products were displaced when in contact with benzene but were not displaced by water.

Variation in Apparent Pore Radius

It will be observed (Table III) that the adhesion tension values of both water and benzene against carbons F and G are low. The question arose as to whether these values represented the true adhesion tensions for these carbons. The pore radius for carbon G, as determined by benzene, was found to be 0.763×10^{-6} cm. Since this radius at least approached the range of molecular influence, it was believed that the very small pores might affect the calculated adhesion tension values. If the method used for measuring pore radii gave values smaller than those actually existing, the adhesion tension values would be decreased in proportion to the error introduced by using the determined radii values.

The determined pore radii of carbons E and F decreased when the packing pressure was increased from 318.3 to 477.5 kg. per sq. cm. Slightly lower adhesion tension values were also observed at the higher packing pressure. These small decreases occasioned by the higher packing pressure may be directly traceable to the increasing error found in the determined pore radii values as the pore sizes became smaller.

Freundlich (9) has stated that a drop of water having a radius of 10^{-6} cm. exhibits a vapor pressure 10 per cent greater than that of a plane surface of water, and for a radius of 10^{-7} cm. this value increases to 100 per cent. He also states:

We must, however, take into account that for such small drops the surface tension has a lower value than for the larger ones. As soon as the drop radius falls within the order of magnitude of the radius of molecular action, or is even smaller, the work required to bring a molecule from the interior of the liquid to the surface becomes smaller, since the number of attracting molecules is smaller than in the case of the completely filled sphere of action which we consider in the case of a larger quantity of liquid.

The conditions would be reversed in the case of a liquid advancing in a capillary tube with a radius of 10^{-7} cm. The surface would be concave, the vapor pressure would be less, and the surface tension would be greater.

Inasmuch as the pore radius for carbon G as given by benzene was of the above-mentioned low order (7×10^{-7} cm.), it was thought that this point should be investigated

further. Liquids with different surface tension values—namely, ether and isobutyl alcohol—were chosen for this purpose. Their surface tension values, determined by the capillary rise method, were 16.55 and 22.42 dynes (at 25° C.), respectively. With the assumption that the surface tensions of these liquids remain unchanged in the capillary pores, the values obtained for the apparent pore radii of selected carbons are given in Table V.

It is evident that these three liquids give the same values (within experimental error) for a pore radius of the order of 10^{-5} cm., but there is a decided discrepancy when a radius of 10^{-6} cm. and less is reached. It was impossible to obtain an equilibrium reading for isobutyl alcohol against carbon G because of the fineness of the pores and the high viscosity of the alcohol.

Table V—Comparison of Pore Radii Values Obtained with Different Liquids

CARBON	PORE RADIUS WITH BENZENE	PORE RADIUS WITH ETHER	PORE RADIUS WITH ISOBUTYL ALCOHOL	DIFF. IN	
				BENZENE- ETHER VALUES	BENZENE- ISOBUTYL VALUES
				Per cent	Per cent
A	7.98×10^{-6}	8.03×10^{-6}	8.01×10^{-6}	+0.66	+0.37
D	1.35×10^{-6}	1.30×10^{-6}	1.25×10^{-6}	-3.7	-7.4
F	1.15×10^{-6}	1.05×10^{-6}	1.00×10^{-6}	-9.9	-13.8
G	7.63×10^{-7}	5.11×10^{-7}		-33.0	

The above pore radii were calculated from the formulation

$$r = 2S/Pg$$

r = radius of the pore

S = surface tension of the liquid

P ($=hd$) = equilibrium displacement pressure

If the values for the pore radii are substituted for r and the equilibrium displacement pressures of ether or of isobutyl alcohol are used for P in the above equation, the calculated surface tensions of these liquids will be greater than their normal values. This increase will be greater with decreasing pore size. It is quite certain that r is the same in each case; therefore, it appears that the surface tensions of the liquids are actually different in the very small pores.

This observed variation in apparent pore radius may also be considered from a different standpoint—namely, that the effective pore radius of a given carbon membrane becomes different when different liquids are used because of a condensed adsorbed layer. While it is generally believed that the attractive forces existing at the interface of two immiscible phases are satisfied to the extent of 95 per cent in the first molecular layer of each phase (8), some experimental work has been carried out which indicates this is not the case. De Waele (15) measured the capillary rise of water in clean tubes, in those containing an invisible film of petroleum jelly, and in a third set which were visibly coated with the jelly. Different values for capillary rise were ob-

tained in each case. Such an experiment leads to the conclusion that when a given phase overlies a second phase, below a certain critical thickness, the overlying phase has properties different from those exhibited by it in bulk. With decreasing thickness it approximates more and more in properties to the phase with which it is in contact.

The critical thickness of a liquid layer in contact with a solid surface is evidently related to the attractive force or adhesion tension existing between these two phases. The thickness of this layer seems to be inversely proportional to the adhesion tension solid-liquid. Bartell and Greager (unpublished work) found that this appeared to be true from experimental data obtained for the oil adsorption values of selected liquids with carbon and with calcium fluoride. From their curves it was noted that the amount of liquid held by the powdered material varied inversely as the adhesion tension of the liquid for the particular solid.

From Table V it will be observed that isobutyl alcohol shows a greater deviation from the benzene values for pore radii than does ether. Unpublished work by Bartell and Osterhof evaluates the adhesion tensions for benzene, ether, and isobutyl alcohol against carbon at 81.08, 59.85, and 56.60 dynes, respectively. Assuming that ether and isobutyl alcohol do have adsorbed layers of increasing thickness on the walls of the carbon pores, smaller values for the apparent pore radii of the carbons would be expected. The percentage difference would also increase as the pore radius decreases. The experimental results seem to bear out this inference.

Thus it appears that the calculated difference in pore radii of very fine pores may be dependent either upon the surface tension values of the liquid used or upon the adhesion values of liquid against the solid constituting the pore wall, or perhaps upon both. In any case it follows that the pressure displacement method is applicable for the measurement of pore radii of capillary tubes only when the radii are greater than about 2×10^{-6} cm. The method does not appear to be suitable for smaller capillaries. Further study along this line should throw some light on the range of molecular attraction and at the same time give information relative to the thickness of the adsorbed layers.

Literature Cited

- (1) Asahara, *Japan. J. Chem.*, **1**, 35 (1922).
- (2) Bartell and Fu, *Colloid Symposium Monograph*, Vol. VII (1929) in press.
- (3) Bartell and Fu, *J. Phys. Chem.*, in press.
- (4) Bartell and Osterhof, *Colloid Symposium Monograph*, Vol. V, 113 (1927).
- (5) Bartell and Sloan, *J. Am. Chem. Soc.*, **51**, 1643 (1929).
- (6) Chaney, *Trans. Am. Electrochem. Soc.*, **36**, 91 (1929).
- (7) Chaney, Ray, and St. Johns, *IND. ENG. CHEM.*, **15**, 1244 (1923).
- (8) Edser, *Brit. Assocn. Advancement Sci.*, 4th Colloid Rept., p. 40 (1922).
- (9) Freundlich, "Colloid Chemistry," p. 46.
- (10) Hulett and Cude, *Bur. Mines, Bull.* **1913**.

- (11) Johnson, *IND. ENG. CHEM.*, **20**, 904 (1928).
- (12) Miller, *J. Phys. Chem.*, **30**, 1162 (1926).
- (13) Nellensteyn, *Chem. Weekblad*, **22**, 291 (1925).
- (14) Ruff, Schmidt, and Albrich, *Z. anorg. allgem. Chem.*, **148**, 313 (1925).
- (15) Waele, de, *J. Am. Chem. Soc.*, **48**, 2760 (1926).

